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(51) Int. Cl.: C09D 004/00, C08G 065/00,  
C09D 171/02, G03F 007/027

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(30) 197 47 890.5 DE 30.10.1997

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(54) UTILISATION D'ESTERS D'ACIDE METHACRYLIQUE DE DIMERDIOLALCOXYLATES EN TANT QUE  
CONSTITUANTS POUR DES REVETEMENTS DURCISSABLES PAR RADIATION

(54) USE OF DIMERDIOLALCOXYLATE (METH)ACRYLIC ACID ESTERS AS CONSTITUENTS FOR RADIATION  
CURED COATINGS

(57)

The invention relates to acrylic or methacrylic  
acids of addition products with 1-80 mol ethylene oxide  
and/or propylene oxide on dimendiols with a majority of  
36-44 C atoms - especially those with a Draize index of  
less than 2.0 - which are highly suitable as  
constituents for radiation cured coatings.





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(30) 1997/10/30 (197 47 890.5) DE  
(54) **UTILISATION D'ESTERS D'ACIDE METHACRYLIQUE DE  
DIMERDIOLALCOXYLATES EN TANT QUE  
CONSTITUANTS POUR DES REVETEMENTS  
DURCISSABLES PAR RADIATION**  
(54) **USE OF DIMERDIOLALCOXYLATE (METH)ACRYLIC ACID  
ESTERS AS CONSTITUENTS FOR RADIATION CURED  
COATINGS**

(57) Esters d'acide acrylique et/ou méthacrylique de produits d'addition de 1 à 80 moles d'oxyde d'éthylène et/ou d'oxyde de propylène sur des dimerdliols ayant principalement 36 à 44 atomes de C, en particulier ceux possédant un indice de Draize inférieur à 2,0, qui sont parfaitement adaptés en tant que constituants pour des revêtements durcissables par radiation.

(57) The invention relates to acrylic or methacrylic acids of addition products with 1-80 mol ethylene oxide and/or propylene oxide on dimerdliols with a majority of 36-44 C atoms - especially those with a Draize index of less than 2.0 - which are highly suitable as constituents for radiation cured coatings.





**PCT**  
 WELTORGANISATION FÜR GEISTIGES EIGENTUM  
 Internationales Büro  
 INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE  
 INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)



<p>(51) Internationale Patentklassifikation 6 :          C09D 4/00, G03F 7/027, C08G 65/00,          C09D 171/02</p>	<b>A1</b>	<p>(11) Internationale Veröffentlichungsnummer: <b>WO 99/23175</b></p> <p>(43) Internationales          Veröffentlichungsdatum: 14. Mai 1999 (14.05.99)</p>
<p>(21) Internationales Aktenzeichen: <b>PCT/EP98/06692</b></p> <p>(22) Internationales Anmeldedatum: 21. Oktober 1998 (21.10.98)</p> <p>(30) Prioritätsdaten:          197 47 890.5      30. Oktober 1997 (30.10.97)      <b>DE</b></p> <p>(71) Anmelder: <b>HENKEL KOMMANDITGESELLSCHAFT AUF          AKTIEN [DE/DE]; Henkelstrasse 67, D-40589 Düsseldorf          (DE).</b></p> <p>(72) Erfinder: <b>HÖPER, Rainer; Kieper Strasse 31, D-40477          Düsseldorf (DE). FIES, Matthias; Dahlienstrasse 26,          D-47800 Krefeld (DE).</b></p>		
<p>(81) Bestimmungsstaaten: <b>CA, JP, europäisches Patent (AT, BE,          CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,          NL, PT, SE).</b></p> <p>Veröffentlicht  <i>Mit internationalem Recherchenbericht.</i></p>		
<p>(54) Title: <b>USE OF DIMERDIOLALCOXYLATE (METH)ACRYLIC ACID ESTERS AS CONSTITUENTS FOR RADIATION CURED COATINGS</b></p> <p>(54) Bezeichnung: <b>VERWENDUNG VON (METH)ACRYLSÄUREESTERN VON DIMERDIOLALKOXYLATEN ALS BAUSTEINE FÜR STRAHLENHÄRTBARE BESCHICHTUNGEN</b></p> <p>(57) Abstract</p> <p>The invention relates to acrylic or methacrylic acids of addition products with 1-80 mol ethylene oxide and/or propylene oxide on dimerdiols with a majority of 36-44 C atoms - especially those with a Draize index of less than 2.0 - which are highly suitable as constituents for radiation cured coatings.</p> <p>(57) Zusammenfassung</p> <p>Acryl- und/oder Methacrylsäureestern von Anlagerungsprodukten von 1 bis 80 Mol Ethylenoxid und/oder Propylenoxid an Dimerdiolen mit überwiegend 36 bis 44 C-Atomen - insbesondere solche mit einem Draize-Index von weniger als 2,0 - eignen sich in ausgezeichneter Weise als Bausteine für strahlenhärtbare Beschichtungen.</p>		



## Use of Dimerdiolalcoxyate (Meth)Acrylic Acid Esters as Constituents for Radiation Cured Coatings

### Field of the Invention

This invention relates to the use of (meth)acrylates of dimerdiol alkoxyates as structural elements for radiation-curing coatings.

### Prior Art

5       Acrylates and methacrylates of 1,6-hexandiol are frequently used as structural elements in the production of radiation-curing coatings. 1,6-hexanediol diacrylate, hereinafter referred to in short as HDDA, is preferably used.

For example US 5,271,968 describes how polycarbonate surfaces  
10       are contacted with coating compositions and the curing process is carried out by exposure to UV light. The coating compositions are preferably based on a polyfunctional acrylate monomer, a photoinitiator and HDDA.

Silane-free radiation-curing acrylate-based compositions are known  
15       from US 5,075,348. In one preferred embodiment, a special triacrylate is mixed with HDDA.

WO 92/17337 describes UV-curing compositions containing various aliphatic acrylate-based urethanes, including inter alia a multifunctional acrylate which acts as a reactive thinner, trimethylol propane triacrylate and HDDA being particularly preferred.

20       HDDA is distinguished by a low viscosity and an excellent capacity to dissolve epoxy, polyester and urethane acrylates. During curing, the HDDA-containing formulations undergo minimal shrinkage so that coatings on metal, glass and plastics, such as PVC, show excellent adhesion. The cured coatings are particularly resistant to abrasion and to chemicals. The



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absence of yellowing and its high gloss predestine HDDA for use in clear coatings for wood and plastics and for clear lacquers on paper. All these properties also make HDDA appear advantageous for pigmented coatings and printing inks.

- 5 HDDA has a vapor pressure of 0.014 mbar at 50°C and a flash point of 79°C (DIN 51794), so that particular precautions have to be taken for transportation, storage and processing.

- Another disadvantage of HDDA is its relatively high skin irritation potential. A measure of this is, for example the so-called Draize index.
- 10 According to "Grundlagen und Rezepturen der Kosmetika" (author: Karlheinz Schrader; publisher: Hüthig; 2nd Edition 1989), page 1029, the Draize test is one of the most common tests for quantifying skin irritation. In the Draize test, the material to be tested is applied for 24 hours to intact and surface-scarified skin of albino guinea pigs. Erythema and
- 15 odema readings are taken after 24 and 72 hours on a scale of 0 to 4 or more. As known to the expert, the skin irritation values of 1,6-hexandiol diacrylate (HDDA) are in the range from about 4.4 to >6.

- EP 62 807 A1 describes diacrylates of addition products of 2 to 6 moles ethylene oxide and/or propylene oxide onto 1,6-hexanediol,
- 20 neopentyl glycol and tripropylene glycol and their use as radiation-curing diluents.

### Description of the Invention

- The problem addressed by the present invention was to provide
- 25 substances which would be suitable for use as structural elements in the production of radiation-curing coatings and which, at the same time, would have an acceptably low skin irritation potential.

- This problem has been solved by (meth)acrylates of dimerdial alkoxylates which are understood to be acrylic and/or methacrylic acid
- 30 esters of addition products of 1 to 80 moles ethylene oxide and/or



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propylene oxide onto dimerdiols predominantly containing 36 to 44 carbon atoms.

Accordingly, the present invention relates to the use of acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide onto dimer diols predominantly containing 36 to 44 carbon atoms as structural elements for radiation-curing coatings.

Dimerdiols are well-known, commercially available compounds which are obtained, for example, by reduction of dimer fatty acid esters. The dimer fatty acids on which these dimer fatty acid esters are based are carboxylic acids which are obtainable by oligomerization of unsaturated carboxylic acids, generally fatty acids, such as oleic acid, linoleic acid, erucic acid and the like. The oligomerization is normally carried out at elevated temperature in the presence of a catalyst of, for example, clay. The substances obtained (dimer fatty acids of technical quality) are mixtures in which the dimerization products predominate. However, small percentages of higher oligomers, more particularly the trimer fatty acids, are also present. Dimer fatty acids are commercially available products and are offered in various compositions and qualities. Abundant literature is available on the subject of dimer fatty acids, of which the following articles are examples:

- Fette & Öle 26 (1994), pages 47-51
- Speciality Chemicals 1984 (May Number), pages 17, 18, 22-24

The dimerdiols on which the dimerdiol alkoxylates to be used in accordance with the invention are based are well known among experts, cf. for example a fairly recent article which discusses inter alia the production, structure and chemistry of dimerdiols:

- Fat Sci. Technol. 95 (1993) No. 3, pages 91-94



According to the invention, preferred dimerdiol alkoxylates are those which are derived from dimerdiols with a dimer content of at least 50% and, more particularly, 75% and in which the number of carbon atoms per dimer molecule is predominantly in the range from 36 to 44.

5       The (meth)acrylates of dimerdiol alkoxylates may be produced by any known relevant methods known to the expert. The are preferably produced as follows: in a first step, the required diol is contacted with ethylene oxide and/or propylene oxide and the resulting mixture is reacted at temperatures of 20 to 200°C in the presence of an alkaline catalyst. In  
10 this way, addition products of ethylene oxide (EO) and/or propylene oxide (PO) onto the particular dimerdiol used are obtained. Accordingly, the addition products are EO adducts or PO adducts or EO/PO adducts with the particular dimerdiol used. In the case of the EO/PO adducts, the addition of EO and PO may be carried out statistically or in blocks. In a  
15 second step, the addition products are converted into acrylates and/or methacrylates.

One embodiment of the present invention is characterized by the use of (meth)acrylates of dimerdiol alkoxylates which contain 2 to 20 moles ethylene oxide per mole dimerdiol. The diacrylates of the adducts of about  
20 2 to 20 moles ethylene oxide with the required dimerdiol are particularly preferred.

Another embodiment of the invention is characterized by the use of (meth)acrylates of dimerdiol alkoxylates which contain 2 to 20 moles propylene oxide per mole dimerdiol. The diacrylates of the adducts of  
25 about 2 to 20 moles propylene oxide with the required dimerdiol are particularly preferred.

A preferred embodiment is characterized by the use of (meth)acrylates of dimerdiol alkoxylates which have a Draize index of less than 2.0 and, more particularly, less than 1.8.



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The present invention is not restricted in any way in regard to the intended application of the radiation-curing coatings produced using the (meth)acrylates of dimerdiol alkoxyates to be used in accordance with the invention.

- 5 Finally, the present invention relates to compositions for the production of radiation-curing coatings containing one or more acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide onto dimerdiols containing 36 to 44 carbon atoms.

10

### Examples

- The testing of a number of (meth)acrylates of dimerdiol alkoxyates according to the invention showed that these substances are generally compounds which represent effective reactive diluents for radiation-curing coatings and which, in addition, are distinguished by only a slight irritation
- 15 potential (Draize values <2).



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**CLAIMS**

1. The use of acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide onto dimerdiols predominantly containing 36 to 44 carbon atoms as structural elements for  
5 radiation-curing coatings.
2. The use claimed in claim 1, characterized by the use of acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide which have a Draize index of less than 2.0.
3. Compositions for the production of radiation-curing coatings  
10 containing one or more acrylates and/or methacrylates of addition products of 1 to 80 moles ethylene oxide and/or propylene oxide onto dimerdiols predominantly containing 36 to 44 carbon atoms.



L4 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2008 ACS on STN  
 AN 1998:535829 CAPLUS  
 DN 129:150132  
 OREF 129:30575a,30578a  
 ED Entered STN: 24 Aug 1998  
 TI Curable dimer diol-derived (meth)acrylate compositions  
 IN Mochizuki, Katsunobu; Kojima, Shiro  
 PA Toa Gosei Chemical Industry Co., Ltd., Japan  
 SO Jpn. Kokai Tokkyo Koho, 4 pp.  
 CODEN: JKXXAF  
 DT Patent  
 LA Japanese  
 IC ICM C08F220-28  
 ICS C09D004-02; C09D011-00; C09D133-14; C09J004-02; C09J133-14  
 CC 42-7 (Coatings, Inks, and Related Products)  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 10218946	A	19980818	JP 1997-31387	19970131 <--
	JP 3861353	B2	20061220		
PRAI	JP 1997-31387		19970131		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 10218946	ICM	C08F220-28
	ICS	C09D004-02; C09D011-00; C09D133-14; C09J004-02; C09J133-14
	IPCI	C08F0220-28 [I,A]; C08F0220-00 [I,C*]; C09D0004-02 [I,A]; C09D0011-00 [I,A]; C09D0133-14 [I,A]; C09J0004-02 [I,A]; C09J0133-14 [I,A]
	IPCR	C09D0004-02 [I,C*]; C09D0004-02 [I,A]; C08F0220-00 [I,C*]; C08F0220-28 [I,A]; C09D0011-00 [I,C*]; C09D0011-00 [I,A]; C09D0133-14 [I,C*]; C09D0133-14 [I,A]; C09J0004-02 [I,C*]; C09J0004-02 [I,A]; C09J0133-14 [I,C*]; C09J0133-14 [I,A]

AB Title heat- or active energy beam-curable comps., useful for water-resistant coatings, inks, adhesives, etc., contain HO(XO)mZO(YO)nH (Z = dimer diol residue; X, Y = C2-4 alkylene; m, n ≥ 0; 2 ≤ m + n ≤ 40) and dimer diol (meth)acrylates. Thus, dehydrating of 100.0 g dimer acid, reacting of 49.4 g ethylene oxide and the dehydrated dimer acid under pressure at 110-120°, esterifying of 100 g of the resulted polyol by 19.9 g acrylic acid to give a diacrylate, sep. esterifying of 100.0 g of the dimer acid by 14.4 g acrylic acid to give another diacrylate, and mixing of 45 g of the former diacrylate, 5 g of the latter diacrylate, 40 g tetraethylene glycol diacrylate, 10 g trimethylolpropane triacrylate, and 1 g benzyl di-Me ketal gave title composition, which was applied on a steel (Bonderite) sheet and UV-irradiated to give a tack-free coating with pencil hardness 2H.

ST curable dimer acid diacrylate dimethacrylate coating; dehydrated dimer acid polyethylene oxide ester; heat curable dimer acid diacrylate coating; UV curable dimer acid diacrylate coating; tetraethylene glycol diacrylate copolymer coating; trimethylolpropane triacrylate copolymer coating; water resistant coating dimer acid diacrylate

IT Coating materials  
 (UV-curable; curable coatings containing polyoxyalkylene dimer acid ester di(meth)acrylates and dimer acid di(meth)acrylate with water resistance)

IT Polyoxyalkylenes, uses  
 RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
 (dehydrated dimer acid ester, acrylate, polymer with tetraethylene glycol diacrylate and trimethylolpropane triacrylate; curable coatings



containing polyoxyalkylene dimer acid ester di(meth)acrylates and dimer acid di(meth)acrylate with water resistance)

- IT Fatty acids, uses  
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
(dimer acids, dehydrated, reaction products with ethylene oxide, diacrylate, polymer with acrylic monomers; curable coatings containing polyoxyalkylene dimer acid ester di(meth)acrylates and dimer acid di(meth)acrylate with water resistance)
- IT Coating materials  
(water-resistant; curable coatings containing polyoxyalkylene dimer acid ester di(meth)acrylates and dimer acid di(meth)acrylate with water resistance)
- IT 79-10-7DP, 2-Propenoic acid, ester with poly(oxyethylene) dehydrated dimer acid ester, polymer with tetraethylene glycol diacrylate and trimethylolpropane triacrylate, uses 15625-89-5DP, Trimethylolpropane triacrylate, polymers with dimer-derived acrylates and tetraethylene glycol diacrylate 17831-71-9DP, Tetraethylene glycol diacrylate, polymers with dimer-derived acrylates and trimethylolpropane triacrylate 25322-68-3DP, dehydrated dimer acid ester, acrylate, polymer with tetraethylene glycol diacrylate and trimethylolpropane triacrylate  
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
(curable coatings containing polyoxyalkylene dimer acid ester di(meth)acrylates and dimer acid di(meth)acrylate with water resistance)
- RN 79-10-7DP  
RN 15625-89-5DP  
RN 17831-71-9DP  
RN 25322-68-3DP

L4 ANSWER 2 OF 3 WPIX COPYRIGHT 2008 THOMSON REUTERS on STN  
AN 1998-501706 [43] WPIX  
DNC C1998-151425 [43]  
TI Curing composition - comprising di(meth)acrylate and di(meth)acrylate of dimer diol  
DC A14; A81; A82; G02; G03  
IN KOJIMA S; MOCHIZUKI K  
PA (TOAG-C) TOA GOSSEI CHEM IND LTD  
CYC 1  
PI JP 10218946 A 19980818 (199843)\* JA 4[0] <--  
JP 3861353 B2 20061220 (200701) JA 6  
ADT JP 10218946 A JP 1997-31387 19970131; JP 3861353 B2 JP 1997-31387 19970131  
FDT JP 3861353 B2 Previous Publ JP 10218946 A  
PRAI JP 1997-31387 19970131  
IPCI C08F0220-00 [I,C]; C08F0220-28 [I,A]; C09D0011-00 [I,A]; C09D0011-00 [I,C]; C09D0133-14 [I,A]; C09D0133-14 [I,C]; C09J0133-14 [I,A]; C09J0133-14 [I,C]; C09J0004-02 [I,A]; C09J0004-02 [I,C]  
IPCR C08F0220-00 [I,C]; C08F0220-28 [I,A]; C09D0011-00 [I,A]; C09D0011-00 [I,C]; C09D0133-14 [I,A]; C09D0133-14 [I,C]; C09D0004-02 [I,A]; C09D0004-02 [I,C]; C09J0133-14 [I,A]; C09J0133-14 [I,C]; C09J0004-02 [I,A]; C09J0004-02 [I,C]  
AB JP 10218946 A UPAB: 20050828  
A curing composition comprising di(meth)acrylate of diol of formula HO-(XO)m-ZO-(YO)n-H (1); Z = dimer diol residue; X, Y = 2-4C alkylene; m and n = integers not less than 0; 2 < or = m + n < or = 40; and di(meth)acrylate of dimer diol.

USE - The curing composition is useful for producing water resisting molded products, coats, inks and adhesives which are required to have water resistance and adhesive (contact) properties with polyolefins.

ADVANTAGES - The curing composition can provide a coat having high water resistance and high contact (adhesive) properties with polyolefins.

MC CPI: A04-B09; G02-A02C4; G02-A04A; G02-A05; G03-B02D1



L4 ANSWER 3 OF 3 JAPIO (C) 2008 JPO on STN  
AN 1998-218946 JAPIO  
TI CURABLE COMPOSITION  
IN MOCHIZUKI KATSUNOBU; KOJIMA SHIRO  
PA TOAGOSEI CO LTD  
PI JP 10218946 A 19980818 Heisei  
AI JP 1997-31387 (JP09031387 Heisei) 19970131  
PRAI JP 1997-31387 19970131  
SO PATENT ABSTRACTS OF JAPAN (CD-ROM), Unexamined Applications, Vol. 1998  
IC ICM C08F220-28  
ICS C09D004-02; C09D011-00; C09D133-14; C09J004-02; C09J133-14  
AB PROBLEM TO BE SOLVED: To obtain a composition which forms a coating film having excellent water resistance and excellent adhesion to polyolefins by mixing a diol di(meth)acrylate with a dimer diol di(meth)acrylate.  
SOLUTION: The diol di(meth)acrylate (A) used is represented by the formula:  $\text{HO}(\text{XO})\langle\text{SB}\rangle_m\langle\text{SB}\rangle\text{-ZO-}(\text{YO})\langle\text{SB}\rangle_n\langle\text{SB}\rangle\text{-H}$  (wherein Z is a dimer diol residue; X and Y are each a 2-4C alkylene; m and n are each an integer of 0 or greater; and  $2 \leq m+n \leq 40$ ). The dimer diol di(meth)acrylate (B) used is a difunctional (meth)acrylic ester prepared by (meth)acryloylating the two hydroxyl groups of the dimer diol. In addition to components A and B, a radical polymerizable monomer (C) copolymerizable therewith may be used. The mixing ratio is desirably such that A:B:C is (5-90):(5-90):(5-90) (weight%). To perform the thermal polymerization of the composition, 0.1-5 pts.weight, per pt.weight total monomer, benzoyl peroxide is used as a polymerization initiator.  
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3. In the drawings, any words are not translated.

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CLAIMS

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[Claim(s)]

[Claim 1] A hardenability constituent containing the following component (A) and (B).

(A): di(meth)acrylate  $\text{HO}-(\text{XO})_m-\text{ZO}-(\text{YO})_n-\text{H}$  (1) of diol expressed with a following chemical formula (1)

(Z is dimer diol residue among a formula, and X and Y are the alkylene groups of the same or different carbon numbers 2-4, m and n are zero or more same or different integers, and it is  $2 \leq m+n \leq 40$ .)

(B): Di(meth)acrylate of dimer diol

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[Translation done.]



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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the hardenability constituent hardened with heat or an activity energy line.

The constituent of this invention is used suitably for a paint, ink, adhesives, etc. with which the mold goods in which a water resisting property is demanded, a water resisting property, and the adhesion over polyolefine are demanded.

[0002]

[Description of the Prior Art] Former and poly ethylene glycol di(metha)acrylate, poly propyleneglycol di(meth) acrylate, Polyester poly (meta) acrylate, polyurethane poly (meta) acrylate, Although polyfunctional (meta) acrylic ester, such as TORIMECHI roll pro pantry (meta) acrylate, was generally used as a raw material of thermosetting or activity energy-line hardening resin, Since these (meta) acrylic ester was hydrophilic nature comparatively, the hardened material did not fit the use of which a water resisting property is required highly. Since they were high polarity, a cured film hardly showed the adhesion over polyolefine.

[0003] On the other hand, the compound which made two hydroxyl groups of dimer diol acryloyl (meta)-ize There is art of using [it being hereafter called die merge ORUJI (meta) acrylate], and raising a water resisting property and the adhesion over polyolefine (JP,3-236349,A). However, there was a problem that this die merge ORUJI (meta) acrylate had an elastic modulus of resin after hardening and low hardness as compared with the above-mentioned general-purpose raw material. And since die merge ORUJI (meta) acrylate was deficient in compatibility with a general-purpose raw material, it was not easy for obtaining the hardened material of the performance which was made to carry out copolymerization of these and the balance of a water resisting property and hardness was able to take.



[0004]

[Means for Solving the Problem] This invention persons came to complete this invention, as a result of inquiring wholeheartedly that an aforementioned problem should be solved. That is, this invention is a hardenability constituent containing the following component (A) and (B).

(A): Di(meth)acrylate  $\text{HO}-(\text{XO})_m-\text{ZO}-(\text{YO})_n-\text{H}$  (1) of diol expressed with a following chemical formula (1)

(Z is dimer diol residue among a formula, and X and Y are the alkylene groups of the same or different carbon numbers 2-4, m and n are zero or more same or different integers, and it is  $2 \leq m+n \leq 40$ .)

(B): Di(meth)acrylate of dimer diol [0005]

[Embodiment of the Invention] The compound of the ingredient (A) in this invention to the polyether polyol (henceforth dimer diol derivative alcohol) expressed with said chemical formula (1). (Meta) By making acrylic acid or (meta) acrylic ester react by esterification or an ester interchange, it is compoundable. Dimer diol derivative alcohol is obtained by making the alkylene oxide of 2-4 carbon numbers add to dimer diol. Namely, as alkylene oxide of 2-4 carbon numbers, Ethylene oxide, propylene oxide, butylene oxide, and a tetrahydrofuran (it omits the following THF) can be used, and the commercial item of the Pes Paul HP-1000 grade marketed, for example from Toagosei, Inc. may be used as dimer diol. In order to make the alkylene oxide which has three membered-rings add to dimer diol, The dimer diol which transformed two hydroxyl groups to the alcoholate with sodium hydroxide or a potassium hydrate is heated at 100-140 \*\*, Dimer diol derivative alcohol is obtained by adding this alkylene oxide of the specified quantity under churning, using a dimer diol alcoholate as an initiator, and carrying out anionic polymerization of the alkylene oxide. When using THF as alkylene oxide, after carrying out cation ring opening polymerization of the THF at about 0 \*\* under existence of a boron trifluoride ether salt, target dimer diol derivative alcohol is obtained by adding disodium salt of dimer diol and suspending a polymerization. The number of the alkylene oxide made to add is 2 mol [ per mol of dimer diol ] or more 40 mol or less. The physical properties of the dimer diol derivative alcohol obtained as it is less than 2 mol approximate with dimer diol, and the effect by addition of alkylene oxide is not revealed. On the other hand, when it increases more than 40 mol, it becomes hydrophilic nature too much and the water resisting property of a hardened material is inferior.

[0006] Next, the above-mentioned dimer diol derivative alcohol is made to react to acrylic acid (meta), methyl acrylate (meta), or (meta) ethyl acrylate. When performing a drying esterification reaction, polyether polyol, acrylic acid (meta), and a catalyst are mixed, and it heats at 60-140 \*\*, and is made to react by making it decompress and dry depending on the case. (Meta) The desirable addition of acrylic acid or (meta) acrylic acid is 2.01 mol or more to 1 mol of polyether polyol. It is not desirable in order that acrylic acid (meta) and unreacted



polyether polyol may remain that it is less than 2.01 mol. As a catalyst, sulfuric acid, p-toluenesulfonic acid, methanesulfonic acid, etc. are used. An addition is 0.1 to 10 % of the weight to the total charge, and is 0.5 to 5.0 % of the weight more preferably.

[0007]After carrying out predrying of the polyether polyol enough, polyether polyol, acrylic ester (meta), and a catalyst are mixed, and you heat at 60-140 \*\*, and make it react by decompressing depending on the case, in performing the ester exchange reaction by dealcoholization. (Meta) The desirable addition of acrylic ester is 2.01 mol or more to 1 mol of polyester polyol. It is preferred to add about 10-1000 ppm of polymerization inhibitor, such as hydroquinone, hydroquinone monomethyl ether, and a 6-t-butyl-2,4-xlenol, in any case of the reaction of the above. To the system of reaction, solvents or these mixed solvents, such as hexane, toluene, xylene, and cyclohexane, can be added. As for the addition of these solvents, it is preferred that it is 80 or less % of the weight to the total charge. Since a reaction will become slow if 80 or less % of the weight is exceeded, it is not desirable.

[0008]2 functional (meta) acrylic ester which made two hydroxyl groups in which the ingredient (B) in this invention is contained in dimer diol acryloyl(meta)-ize Although it is by [it is called below die merge ORUJI (meta) acrylate], this is obtained by making dimer diol acryloyl(meta)-ize by the same method as the above-mentioned ingredient (A).

[0009]It combines with the above-mentioned ingredient (A) and (B) in this invention, and they are them and a copolymeric radical polymerization nature monomer. It can use [this is called ingredient (C) below]. As an ingredient (C), acrylic acid (meta), methyl acrylate (meta), (Meta) Ethyl acrylate, butyl acrylate (meta), acrylic acid (meta)-2-ethylhexyl, (Meta) Monofunctional vinyl compounds, such as acrylic acid lauryl, acrylic acid (meta) stearyl, and N-vinyl pyrrolidone, 1,6-hexanediol di(metha)acrylate, 1,9-nonane JIORUJI (meta) acrylate, Die merge ORUJI (meta) acrylate, poly ethylene glycol di(metha)acrylate, Poly propyleneglycol di(meth) acrylate, polyurethane poly (meta) acrylate, ARONIKKUSU (made by Toagosei) of polyfunctional (meta) acrylate, such as polyester poly (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, and pentaerythritol poly (meta) acrylate, or marketing, etc. are mentioned.

[0010]The desirable rates of the above-mentioned ingredient (A) in this invention, (B), and (C) are (A):(B):(C) = 5 - 90:5 - 90:5 - 90 (% of the weight). A mixed monomer does not become it uniform that (A) is less than 5 % of the weight, the water resisting property which was excellent in the hardened material in (B) being less than 5 % of the weight, and adhesion over polyolefine cannot be given, and the toughness of resin is not accepted that (C) is less than 5 % of the weight. If needed, the hardenability constituent of this invention which makes the above-mentioned ingredient indispensable can blend the additive agent of others, such as a polymerization initiator, and can harden it by thermal polymerization or the polymerization by an activity energy line.



[0011]When carrying out thermal polymerization, redox systems, such as azo compounds, such as peroxide, such as benzoyl peroxide and lauroyl peroxide, azobisisobutyronitrile, and azobisvaleronitrile, or benzoyl peroxide / dimethylaniline, can be used as a polymerization initiator. An addition is 0.1 to 5 weight section to total monomers. Polymerization temperature is usually 50-140 \*\*, and, in the case of a redox system, can polymerize also near a room temperature. As an example of the polymerization by an activity energy line, the polymerization by ultraviolet rays and the polymerization by an electron beam are mentioned. When performing the polymerization by ultraviolet rays, benzyl dimethyl ketal, benzophenone, an acetophenone derivative, etc. are used as an initiator. On the other hand, in the polymerization by an electron beam, it usually polymerizes with a non-catalyst.

[0012]Hereafter, a reference example, an example, and a comparative example are given, and this invention is explained still more concretely. The dimer diol used in each following example is Pes Paul HP-1000 (henceforth DD) marketed from Toagosei, Inc.

#### [Reference example 1]

(1) In the autoclave in which dimer diol derivation alcohol carried out the manufacture nitrogen purge, DD(hydroxyl value: 197 mgKOH/g) 100.0g (0.187 mol) and the 40% of potassium hydrate solution 52.4g (0.374 mol) were added, by 100 \*\* and pressure 5mmHg, drying was performed for 3 hours and the reactant with a water content of about 100 ppm was obtained. It applied to this for 4 hours, and 49.4 g (1.122 mol) of ethylene oxide was made to add and react to the above-mentioned reactant set as 110-120 \*\* by (5kg/cm<sup>2</sup>) under application of pressure at it. Then, it cooled at 60 \*\*, and decompressed to 10mmHg, and residual ethylene oxide was removed. After chloride neutralized the resultant, drying and filtration were performed and 143g of polyether polyol A (only henceforth the polyol A) of hydroxyl value 140.8 mgKOH/g (number average molecular weight: about 800) was obtained. The polyol A turned out to be per 1 mol of DD, and the polyol which 6.0 mol of ethylene oxide added by <sup>1</sup>H NMR analysis.

[0013](2) The diacrylate A 100[ manufacture profitable \*\*\*\* dimer diol derivation alcoholic ] g (0.125 mol) Hits, The water which carries out heating churning and is generated at 110 \*\* was distilled off out of the system, having taught the acrylic acid 19.9g (0.276 mol), 1.2 g of p-toluenesulfonic acid, 0.01g of monomethyl hydroquinone, and 120 g of toluene to the flask, and blowing air. It cooled to the room temperature in the place which made water distill for about 6 hours. The water layer was removed, after adding sodium hydroxide (15.0g) 10% to the above-mentioned reaction mixture and agitating to it. It washed 3 times with water (50.0g). 0.01 g of monomethyl hydroquinone was added to this, by 80 \*\* and 10mmHg, distillation under reduced pressure of the toluene was carried out, and the diacrylate A was obtained.

[0014]

#### [Reference example 2]



(Composition of dimer diol diacrylate)

100g (0.091 mol) of dimer diol hit, acrylic acid 14.4g (0.200 mol) use of was done, and other ingredients were used like the reference example 1, and manufactured dimer diol diacrylate by the same operation as the reference example 1.

[0015]

[Example 1- and the comparative examples 1-2] After painting the hardenability constituent produced by blending each ingredient shown in Table 1 to a BONDE light board by bar coater #10, it irradiated with ultraviolet rays on the coat 30 times the speed for 10-m/using the condensed type high-pressure mercury lamp (80 W/cm, lump height: 10 cm). A feeling of finger touch of the obtained cured film and evaluation of pencil hardness were performed, and the result was shown in Table 1. The "part" in Table 1 is a "weight section." After slushing a hardenability constituent into the spacer (5cmx5cmx1mm) covered from both sides with the PET film, this sample is irradiated with ultraviolet rays twice (one rear surface each) 30 second respectively with a parallel beam type high-pressure mercury lamp (60 W/cm, lump height: 30 cm). It removes and irradiates with a PET film twice (one rear surface each) 30 second respectively. Water was made to immerse the obtained hardened material at 23 \*\* for 48 hours, water absorption (percentage of the weight increment by the immersion on the basis of the sample weight before immersion) was measured by the weight change, and the result was written together to Table 1.

[0016]

[Effect of the Invention]The hardenability constituent of this invention can form the coat which has the outstanding water resisting property and the adhesion over polyolefine, and is used suitably for the field of mold goods, a paint, ink, adhesives, etc.

[0017]

[Table 1]



	実施例 1	実施例 2	比較例 1	比較例 2
ジ・アクリレート A (部)	45	20	—	—
タ・イマ・ジ・オールジ・アクリレート	5	30	—	50
テトラ(エチレング・リコール)ジ・アクリレート	40	40	80	40
トリメチロールプ・ロハ・ントリアクリレート	10	10	20	10
ベンジ・ルジ・メチルケタル	1	1	1	1
硬化物の外観	透明	透明	透明	白濁
指触感	○	○	○	△
鉛筆硬度	2H	2H	3H	F
吸水率 %	0.3	<0.1	2.8	1.0

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[Translation done.]